DEPOSITION OF SILICA FILMS BY THE

GLOW DISCHARGE TECHNIQUE

by

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ABSTRACT

Noncrystalline SiO_2 films were deposited on various substrates at low temperatures and pressures by decomposing tetraethoxysilane in an R.F. induced oxygen plasma. The rate of deposition was controlled by physical adsorption; the apparent heats of adsorption of silica on NaCl, Pt, fused SiO_2, Al, and Al_2O_3 were determined. A mechanism for formation is presented. The decomposition of the tetraethoxysilane obeyed a first order rate law. The specific rate constant was calculated at 310°C and 250 microns pressure.

Studies and utilization of thin films, both metallic and non-metallic, have experienced considerable growth in the last decade. Silica films, in particular, have enjoyed a multitude of applications. For instance, masks for semiconductor devices or dielectric capacitors for miniaturized solid state circuits are conveniently formed with glassy silica. Silica films can be formed by many techniques, (1) most of which necessitate relatively high temperatures. The "glow discharge" method to be described facilitates the deposition of glassy silica films from the vapor phase at low temperatures and pressures by the decomposition of tetraethoxysilane in an oxygen plasma. Alt et al (2) and Ing and Davern (3), for example, have prepared amorphous silicon oxide films of unknown stoichiometry in one form of the glow discharge technique. We have modified this technique by the use of a microwave glow-discharge. The effects of temperature, pressure, organic flow (evaporation) rate, and nature of the substrate on the rate of film growth are reported in this paper.

EXPERIMENTAL

Materials

Tetraethoxysilane, $C_2H_5O)_4Si$, and tetraethysilane,

$(C_2H_5)_4Si$, were obtained from Metallomer Laboratories, Maynard, Mass., and were of > 98% purity.

Apparatus

The glow discharge apparatus consisted basically of a modified bell jar which could be maintained at low pressures under sustained gas flow. A schematic drawing of the flow system is illustrated in Figure 1. Molecular oxygen was admitted to the system through a 0.003" precision bore capillary which was positioned between the legs of a mercury manometer. With a pressure differential of 770 mm., the incoming gas flow rate was experimentally determined to be 1.76 ± 0.05 cm^3/minute. A pyrex tube one inch in diameter served as the glow discharge chamber. The electrodeless discharge was produced with a Raytheon PGM-10 Microwave Generator. This unit could supply 100 watts of microwave energy at a fixed frequency of 2,450 megacycles/sec. The R.F. energy, as generated in a magnetron, was transferred by a coaxial cable to the antenna (labelled wave guide in Fig.1) for dissipation.

The predominant specie formed in a low energy oxygen discharge has been identified as atomic oxygen in the ground state (4, 5). The energized species thus formed were allowed to flow into the bell jar through a 0.5"

diameter pyrex tube. By the use of a nitrogen dioxide-titration technique (4), it was estimated that about 10% of the flowing molecular oxygen entered the bell jar as atomic oxygen. Tetraethoxysilane (as contained in a graduate cylinder immersed in a constant temperature bath) was introduced into the bell jar through a 3/16" diameter pyrex tube under its own vapor pressure. A constant temperature bath could be maintained inside an insulated two liter dewar flask for long periods. The metal-organic evaporation rate (flow rate) at any particular bath temperature could be altered by adjusting a one millimeter bore teflon stopcock, which served as the inlet valve into the bell jar.

Initial experiments indicated that when the substrate was maintained at temperatures below 180°C, water was present in the films.(6) Two nichrome-wound furnaces were therefore designed to "contain" the gas reaction. The majority of the studies were performed inside an aluminum furnace 2-¼" in diameter and 4" long. A fused silica cylinder 1-3/8" in diameter and 2-½" long was used as the second furnace core. In each case, the top of the furnace was covered with a transite lid. The constant temperature zone for these furnaces extended one centimeter above and

below the gas inlet port with a maximum radial temperature

variation of $\pm$ 5°C for points one centimeter from the

cylinder axes. The substrate temperature was measured under

deposition conditions with a calibrated chromel-alumel thermo-

couple. The corresponding furnace wall temperature was

noted and used in subsequent experiments for temperature

control.

The ultimate vacuum achieved in the glow discharge

system was 240 microns with an oxygen flow rate of 1.76 $cm^3/$

minute. Periodic pressure measurements were made with a

Stokes McLeod gauge and did not include the partial pressures

of condensable gases such as water. Two liquid nitrogen cold

traps were placed in the line leading to the vacuum pump

in order to remove objectionable materials from the system.

A thermocouple vacuum gauge was employed to monitor the

exhaust pressure on a continuous basis.

Film Deposition

Depending on the nature of a particular experiment, the

substrate on which a film was to be deposited was suspended

from either a quartz helix balance or the furnace roof.

Preliminary infrared transmission studies were conducted

for the purpose of identifying the film deposited; wafers

of NaCl and KBr were used as substrates. The substrates

employed in the kinetic studies were hung from the fused

silica balance and were limited in weight by the load ca-

pacity of the balance, which was 20 milligrams. For this

work, the desirable weight of a specimen was arbitrarily set

at 10 ± 1 milligrams. The fused silica substrates were of

irregular shape and approximately 0.75 cm. in diameter.

Aluminum and platinum foils were available in the form of

one centimeter diameter pans. To examine the effects of

Al_2O_3 on the deposition rate, an alumina (Lucalox) sub-

strate was prepared by grinding a wafer of the material to

a thickness of 0.002". A sodium chloride disc one centimeter

in diameter was formed by the compaction of NaCl powder in

a die at 12,000 pounds sq. in. pressure.

With the exception of the sodium chloride substrate,

the general cleaning procedure adopted consisted of the

rapid dipping of the specimens into a 48% solution of hydro-

fluoric acid, followed by rinsing with distilled water. All

substrates were positioned in the reaction vessel in the

same manner - with their wide dimension perpendicular to

the gas inlet tube. (The thin dimension is perpendicular

to the inlet tube in Figure 1). Approximately one hour

was required for the furnace to attain thermal equili-

brium. During the period when the furnace temperature was
increasing, the system was purged with tank purity oxygen
gas supplied by the Linde Company (assay 99.7% oxygen). The
average dew point of the gas was determined to be -56°F
(0.071 mg. water/liter) and was relatively constant from
cylinder to cylinder. When the furnace had reached thermal
equilibrium, the glow discharge was initiated with a spark
coil and the substrate was bombarded with atomic oxygen
for 10-15 minutes as an additional cleaning procedure. In
this work, the microwave generator was operated at 90% of
its rated power output. On opening the organic inlet valve,
approximately five minutes were required for the system to
return to thermal equilibrium. The temperature variation
thereafter was limited to $\pm$ 2°C. The total pressure of the
glow discharge system (excluding condensable gases) increased
by about 10% and was reproducible for specific organic evapo-
ration rates.

The fused silica balance used in this study had a
sensitivity of 1 cm/mg. (Microchemical Specialties Co.
Berkeley, California) A weight of one milligram caused an
extension of 10.1 millimeters from zero, and 98.6 milli-
meters after an appropriate load of 10 mg. (approximate
substrate weight). A typical weight gain experiment would

extend the helix by 1-2 millimeters. Over this limited working range, the helix extension per unit weight gain was linear. A Bausch and Lomb Optical Reader was employed to determine the cumulative weight of the film deposited. The telescope combined a 5 mm. diameter objective field with a filar micrometer eyepiece containing a cross-line divisible to 5,000 parts. The minimum extension detectable with this arrangement was 0.005 mm., which corresponded to a weight gain of approximately 0.5 micrograms (or a 15 $\overset{\circ}{A}$ layer of SiO_2 on a one centimeter diameter pan). Measurements were made every 5 or 10 minutes for the duration of the deposition period, which generally lasted from $1\frac{1}{2}$ to 2 hours. The incoming gas flow rate was slow enough so that the substrate was stable in the position perpendicular to the flow inlet tube. The damping period of the helix was practically instantaneous - no oscillation was observed under equilibrium conditions. At the end of an experiment, the volume of the metal-organic evaporated was measured to $\pm$ 0.025 cm^3.

RESULTS AND DISCUSSION

Gas Analysis

A quantitative analysis of the gaseous reaction products was made by mass spectrometry. The results are shown in Table 1. The decomposition is seen to produce extensive

amounts of water. With an organic evaporation rate of 0.12 cm^3/hr., the partial pressure of water for a gas sample collected from the outlet system was about 30 per cent of the total pressure. The water produced in this manner could be chemically incorporated into the oxide films when the substrates were held below a certain temperature, which depended on the organic flow rate (6). For example, with a $(C_2H_5O)_4Si$ evaporation rate of 0.015 cm^3/hr., silicic acid was observed to form below 180°C, as determined by infrared transmission studies. The acid exhibited a characteristic absorption band at approximately 11 microns. In addition, the major Si-O absorption mode was modified by a "shoulder" at approximately 8.5 microns. When the evaporation rate was increased to 0.15 cm^3/hr., the presence of acid was observed at temperatures as high as 290°C.

Film Evaluation

The refractive indices of the silica. films were measured as 1.458 $\pm$ .002, by the "Becke Line" method. Specimens were obtained from the substrate and/or gas inlet tube. The index of refraction for high purity silica glass (supplied by the General Electric Company) was measured as 1.458 $\pm$ .002, in good agreement with the film values. The films were isotropic when observed with polarized light and were

amorphous by x-ray diffraction. A comparison of the infra-
red absorption spectrum of a silica film deposited on a
NaCl substrate with that of fused silica glass is shown in
Figure 2. The infrared band at 1,080 cm^{-1} has been identi-
fied as a definite Si-O-Si bond stretching vibration. The
band at 800 cm^{-1} is not well understood, but has often been
associated with the occurrence of ring groups in the glassy
structure. The major Si-O stretching mode for the film has
shifted to a somewhat lower frequency. A similar shift of
the same .absorption band has been reported for samples of
silica glass which were highly stressed and densified by
either the application of very high pressures or by neutron
irradiation (7, 8). Pliskin and Lehman (9) have shown that
porosity in the films and bond strain can affect the spec-
trum in the same manner. It is also possible that a vari-
ation of the Si-O-Si angle or a change in the orientation
of silica tetrahedra could occur during the buildup of a
silica network by vapor deposition and cause a shift.

The relative thickness of the films deposited on the
front and back faces of a one-inch diameter NaCl wafer was
determined by measuring the area under the main infrared
absorption band. The spectrum for both films was recorded
and then re-examined after one film had been removed from

the wafer. The area under the Si-O band for both films was
approximately twice the area recorded for the single film.
In this way, the films were determined to be of approximately
the same thickness, which showed that the "silicon-oxygen
specie" concentration in the gas phase immediately surround-
ing the substrate was relatively uniform. The thin silica
films (5,000 Å) adhered well to all of the substrates.
Films three microns in thickness were readily deposited
onto the aluminum, fused silica, or alumina substrates,but
spalled off from platinum foil when the thickness exceeded
about 5,000 Å. This behavior could not be attributed to the
differences in the thermal expansion coefficients of the
substrates. Some of the films were re-examined after three
weeks exposure to the atmosphere. The refractive indices
and infrared absorption spectra were unchanged.

Kinetics of Deposition

The decomposition of the $(C_2H_5O)_4Si$ was studied in a
flowing system maintained at 250 ± 10 microns pressure. By
this method, the reaction products were removed from the
system and the secondary reactions were substantially re-
duced. The effect of temperature on the deposition rate of
the glassy silica films was studied with a constant organic
evaporation rate of 0.15 ± 0.01 cm^3/hr. The effect of minor

pressure variations was found to be negligible. For example when the total gas pressure was increased to 500 microns (by the use of a valve leading to the vacuum pump), no change was detected in the rate of deposition. However, any further increase of the total pressure rapidly decreased the rate of deposition due to (1) poisoning effects from the reaction products and (2) an increased recombination rate of the oxygen atoms in the bulk phase. Under equilibrium conditions, the rate of deposition was constant, as shown in Figure 3. The variation of the deposition rate with temperature could be described by the Arrhenius equation above 290°C:

$$r = A \exp (-H/RT) \tag{1}$$

where
- r = deposition rate (mg/cm^2/min.)
- A = a constant
- H = apparent heat of adsorption -(kcal/mole)
- R = gas constant (1.99 cal/degree/mole)
- T = substrate temperature (°K)

The relationship between logarithm r and reciprocal temperature is shown in Figure 4. The data have been spread to show the temperature dependence of the deposition rate on each substrate. From this figure, it is apparent that the deposition rate is relatively insensitive to temperature

below about 290°C. Above this temperature, the rate de-
creases with increasing temperature. In addition, the rate
of deposition on sodium chloride, fused silica, and plati-
num is equivalent, but different from the deposition rate on
aluminum and alumina (for all practical purposes, the
aluminum substrate can be considered as alumina, since a
surface layer of the oxide is always present). As pre-
viously mentioned, silicic acid was identified as a major
constituent in the films formed below 290°C when the organic
evaporation rate was 0.15 cm^3/hr. The relatively constant
deposition rate noted in Figure 4 below approximately 290°C
can be associated with this acid formation. However, this
does not imply that the acid is formed on the substrate
surface. Brady (10) has stated that both $Si(OH)_4$ and
$Si_2O(OH)_6$ probably exist in the vapor phase when steam is
equilibrated with a siliceous molecule at relatively high
pressures and Straub (11) has suggested that silicic acid
can be formed in the vapor phase. In addition, Brewer and
Elliott (12) have proposed that $Si(OH)_2 \cdot 3H_2O$ can exist as
a volatile specie. It is conceivable, therefore, that the
silicic acid observed in the present study could be formed
in the vapor phase. Since about 30% of the total gas pres-
sure of the system was due to the water formed in the

decomposition process, it was apparent that the mixture of "silicon-oxygen species" and water molecules or "hydrated silicon-oxygen species" bombarding the substrate surface was well in excess of the number which could be deposited. It is proposed that a maximum adsorption of the mixture occurs until a temperature is reached when the incorporation of water into the film is thermodynamically unfavorable (in this case, 290°C). Above this temperature, silica is deposited. Supporting evidence for this mechanism is offered by the work of Hockey and Pethica (13), who reported that the hydration of silica made by burning $SiCl_4$ in a hydrogen-oxygen mixture occurred as chemisorbed hydroxyl groups bonded to surface silicon atoms. In their studies, the surface hydroxyl groups could be removed from the silica surface by heating in the range 200-400°C.

The decrease in the deposition rate above 290°C is characteristic of an adsorption-controlled process. In order for the free energy of the system to decrease, heat must be evolved, and the rate of an exothermic process will generally decrease with increasing temperature. From an atomistic viewpoint, in this study, the "silicon-oxygen specie" could be imagined to possess a mean lifetime in which to select a site on the substrate surface. As the

temperature is raised, more kinetic energy would be imparted to the specie, and the mean lifetime for adsorption would be decreased. Klerer (14) has proposed a similar mechanism for the deposition of organic polymer films of silicon below 250°C.

The apparent heats of adsorption of silica glass on the various substrates were calculated from the slopes of the lines in Figure 4. A regression analysis of the data was made to determine the most probable slopes and the standard deviations. The apparent heat of adsorption of silica on the fused silica, NaCl, and platinum substrates was calculated to be 12.7 kcal/mole, with a standard deviation of 0.2 kcal/mole. For the aluminum or alumina substrates, the apparent heat of adsorption was calculated to be 9.5 kcal/mole, with a standard deviation of 0.3 kcal/ mole. The magnitudes of the heats of adsorption are typical of those reported for physical adsorption processes; e.g., the heat of adsorption of CO_2 on silica gel is approximately 7.1 kcal/mole; that of water on charcoal is about 10.0 kcal/mole (15).

In general, it may be stated that the heat of adsorption of the same adsorbate on different substrates is approximately the same (16). For multimolecular adsorption,

the initial substrate surface is masked after several mono-layers of adsorbate have been deposited. For example, in this study all subsequent condensate will fall on a SiO_2 layer rather than the original substrate surface. For this reason, the rate of deposition on all substrates should be similar. The difference in the apparent heat of adsorption of silica on the platinum, silica, or NaCl substrates and the alumina or aluminum substrates is real and much larger than the limit of error imposed by the standard deviations. It was concluded that the nature of the aluminum oxide surface was responsible for the difference in the apparent heats of adsorption observed. The reaction of alumina with silica to form a compound was not considered, since the rate of deposition of silica became constant soon after the metal-organic vapor was admitted to the reaction furnace. In addition, the rate of such a reaction would probably be quite slow at 300-400°C.

The chemical nature of a substrate surface has been reported to influence a number of processes, even though the surface is covered with many molecular layers of ad-sorbate. For example, a mica substrate will affect the crystallization behavior of ammonium iodide through a film of cellulose acetate or rubber 1000 Å in thickness (17).

TABLE I

GAS ANALYSES

	Gas Outlet Sample	Furnace Sample
% O_2	12	7
% CO_2	30	23
% CO	38	52
% H_2	20	18
H_2O	80 μ /250 μ *	Trace
$(C_2H_5O)_4Si$	Trace	Trace
CH_4	Trace	- - -
Alcohols	- - -	- - -

* Total gas sample pressure = 250 μ
Partial pressure of water = 80 μ
Partial pressure of noncondensable gases=
170 μ

$(C_2H_5O)_4Si$ evaporation rate = 0.12 cm^3/hour
Oxygen flow rate = 1.76 cm^3/minute
Furnace temperature = 310 °C

A similar observation was made in the present study when a potassium bromide substrate was used in place of a NaCl disc for the identification of silicic acid below 290°C. Silicic acid inclusions were not detected by infrared analysis when the films were formed on NaCl substrates held at 290°C (for organic evaporation rates up to 1 cm^3/min.). However, under similar conditions of temperature and pressure, but with an altered organic evaporation rate of 0.15 cm^3/hour, silicic acid was observed to form in the film deposited on a KBr substrate. (The NaCl and KBr substrates were single crystals and showed no evidence of water by infrared analysis prior to these experiments). From this experiment, it was concluded that the hydrophilic nature of the KBr surface could account for the selective absorption of water into the silica structure.

The adsorptive properties of an oxide surface are usually dependent on the degree of hydration and the chemical state of the hydrated surface (when the adsorbates can form hydrogen bonds). Peri and Hannon have reported that both hydroxyl groups and water molecules are held on the surfaces of γ-alumina (18). In their work, the water molecules were desorbed on heating in a vacuum to 400°C, but about 40% of the surface area remained covered with hydroxyl

groups. A similar state of hydration probably existed on the surface of the alumina disc used in this study. In the same way that the KBr substrate adsorbed water, it is proposed that a hydrated alumina surface would tend to incorporate further hydroxyl groups into the silica film. The adsorption of hydroxyl groups would account for the difference in the apparent heat of adsorption observed with the alumina surfaces.

Reaction Order and Specific Rate Constant

The deposition rate of silica was directly proportional to the concentration (evaporation rate) of tetraethoxysilane for evaporation rates below 0.13 cm^3/hour. This relationship is illustrated in Figure 5 for silica glass deposited onto platinum and aluminum foil. For evaporation rates below 0.13 cm^3/hour, it is evident that the decomposition of the metal-organic obeyed a first order rate law of the form:

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} \tag{2}$$

where
k = specific rate constant, sec^{-1}
t = reaction time, sec.
a = metal-organic evaporation rate, cm^3/hr.
x = metal-organic decomposition rate, cm^3/hr.

For evaporation rates in excess of 0.13 cm^3/hr., the substrate area was rate-limiting.

The maximum amount of tetraethoxysilane which could be decomposed in the oxygen plasma was not determined in this investigation. However, an indication of the amount of tetraethoxysilane decomposed could be obtained from the total pressure of the system. A slight, but progressive increase in pressure was noticed when the organic evaporation rate was increased from 0.13 cm^3/hr. to 0.16 cm^3/hr. Hence, the amount of organic decomposed was not rate-limiting. The deposition rate on the alumina substrate was greater than that on the platinum substrate because of a variation in the "silicon-oxygen specie" concentration (the volume of the fused silica furnace was about one-third of that for the aluminum furnace with the same organic flow rate). The incorporation of hydroxyl groups into the silica film deposited on the alumina substrate would account for the difference in the slopes of the two lines in Figure 5, as previously discussed.

In order to apply equation (2) to a flow system, Frost and Pearson (19) redefined the time variable as t = V/u, where V is the volume of the reaction chamber and u is the gas flow rate. The time variable V/u was a measure of the time that a gas reactant would spend in passing through the reaction vessel. In deriving this equation, it was

assumed that the rate of the gas flow through the reaction

chamber was constant and that the gases did not mix. An

approximate value of the specific rate constant for the

decomposition of tetraethoxysilane can be calculated from

this latter equation. The following assumptions were made:

a) the rate of gas flow through the furnace was constant
b) gas mixing did not occur
c) the total reaction took place in the furnace
d) the inlet gas temperature was similar to the furnace temperature
e) the ideal gas law was applicable to both oxygen and tetraethoxysilane.

These assumptions are not unreasonable. The constant silica

deposition rate would indicate that the flow rates were

fairly constant. The reactant gases were fed into the

furnace through individual inlet tubes and did not premix.

The rate of deposition of silica rapidly decreased as the

substrate was lowered in the reaction furnace, which showed

that the reaction took place predominantly in the furnace

vessel. The inlet gas temperature was similar to the fur-

nace temperature because the radial temperature variation

in the furnace was not appreciable under flow conditions.

For the temperature and pressure conditions of the experi-

ment, oxygen does not deviate appreciably from the ideal

gas law. The oxygen flow rate was much larger than that

of the metal-organic vapor, so that even if the ideal gas

law were not obeyed by the latter, the effect on the calculations involved would be minor.

A calculation of the rate constant was made for the fused silica furnace (Volume = 62.5 cm^3) for an organic evaporation rate of 0.12 cm^3/hour. The amount of tetraethoxysilane decomposed was estimated from a knowledge of the reactant products and their respective concentrations. In view of the reaction products, it was evident that the oxidation of the tetraethoxysilane was quite complete. From Table 1, the total number of moles of oxygen combined as either carbon monoxide or carbon dioxide is seen to be similar for the two gas samples; the amount of oxygen present in each case would be equivalent if the condensable water vapor pressure was taken into account (O_2 = 12% based on non-condensable gas pressure, O_2 = 8% including water pressure). By comparing the total number of moles of oxygen consumed (including oxygen available from the tetraethoxysilane) with the amount of oxygen required for the complete combustion of the tetraethoxysilane according to the analysis in Table 1, it was estimated that 85% of the tetraethoxysilane was decomposed under equilibrium conditions. A 10% error in this estimate would cause a 37% error in the specific rate constant.

The total gas flow rate was calculated by assuming that the ideal gas law held for both the oxygen and tetraethoxysilane. The gas flow rate determined in this way was 1.96 cm^3/min. at 25°C and one atmosphere pressure. This flow rate was corrected for a temperature of 310°C (furnace temperature) and 250 microns pressure by the application of Boyle's law. The values were then substituted into Equation (2) and the specific rate constant was calculated to be 5.85 sec.$^{-1}$. In view of the assumptions required for this calculation, the limits of error were estimated to be ± 50%, or k = 6 ± 3 sec.$^{-1}$ at 310°C and 250 microns pressure.
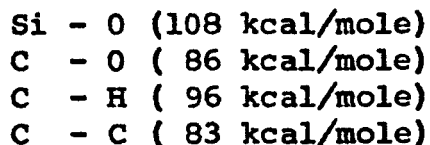
Mechanism of Film Formation

In this study, the energy necessary for the decomposition was supplied in the form of an oxygen plasma produced in a glow discharge. The predominant specie formed in an oxygen discharge has been identified as atomic oxygen in the ground state (4, 5). The homogeneous recombination of atomic oxygen in the gas phase is accompanied by the release of 59.1 kcal/mole of atomic oxygen (20); it was presumed that the amount of energy liberated when the oxygen atoms interacted with the metal-organic molecules was of a similar order of magnitude.

A mechanism for the decomposition can be postulated

from a consideration of the bond energies within the

molecule and the reaction products. The tetraethoxysilane

molecule can be represented as:

```
     R        H   H
     |        |   |
R -  Si - 0 - C - C - H   where R = (C2H5O)
     |        |   |
     R        H   H
```
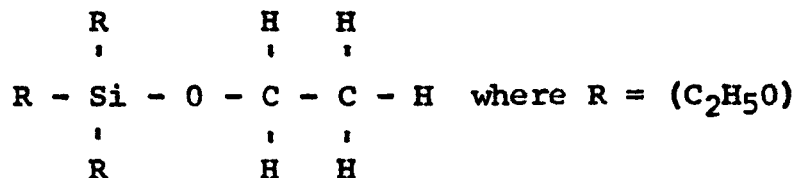
The bond energies involved are taken from Cottrell (20)

and are as follows:

$$
\begin{aligned}
&Si - 0 \quad (108 \text{ kcal/mole}) \\
&C \ - 0 \quad (\ 86 \text{ kcal/mole}) \\
&C \ - H \quad (\ 96 \text{ kcal/mole}) \\
&C \ - C \quad (\ 83 \text{ kcal/mole})
\end{aligned}
$$

From this data, it was apparent that the Si - 0 bond

would be the least likely to rupture. The C - 0 bond is

comparatively weaker and rupture of this bond would free

a C_2H_5 group. At the same time, hydrogen could be detached

from the molecule. Although the subsequent reactions are

too numerous to list, it is probable that the following

preliminary reactions are among those which occurred:

$$C_2H_5 \rightarrow C_xH_y \tag{3}$$

$$H + H \rightarrow H_2 \tag{4}$$

$$C_xH_y + 0 + O_2 \rightarrow CO_2 + H_2O \tag{5}$$
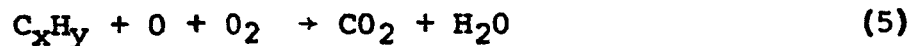
To determine whether the decomposition was influenced

by the chemical nature of the furnace vessel, experiments were conducted in both a fused silica furnace (Volume = 62.5 cm^3, Surface = 81 cm^2) and an aluminum furnace (Volume = 202 cm^3, Surface = 181 cm^2). The apparent heats of adsorption of silica on an alumina substrate were found to be similar. (See Figure 4). This indicated that the mechanism of the decomposition was independent of the reaction chamber. In order to establish whether thermal energy contributed to the decomposition rate, two weight gain experiments were conducted at 400°C without a glow discharge and under both static and dynamic conditions. No decomposition or adsorption of the organic vapor occurred on a platinum substrate during an eight hour period, which demonstrated that silica was not being deposited under these conditions.

Ing and Davern (3) have deposited silicon oxide films of unknown stoichiometry by decomposing tetraethoxysilane in a glow discharge operated at 0.5 megacycle. A mechanism for film growth was proposed, based on the high energy particle bombardment decomposition of tetraethoxysilane in the gas phase to yield silicon oxide clusters. It was thought that the clusters were subsequently deposited onto a substrate surface and that any attached organic groups

were then further dissociated.

Glassy silica films were prepared in our studies by decomposing tetraethoxysilane in an argon plasma. The index of refraction of the films was measured as 1.458 ± .002, in agreement with the value for silica glass. The infrared adsorption spectra of these two noncrystalline solids were also similar, and exhibited absorption bands at 9.2 and 12.5 microns. This experiment showed that the "silicon-oxygen specie" was directly available from the organic molecule. Evidently the metal-organic molecule can absorb sufficient energy to cause bond rupture and a "silicon-oxygen specie" is formed. The rate of film growth in the argon plasma was exceedingly slow; a film of approximately 2,000 Å in thickness was deposited after 6 hours. This suggested that the rate of the decomposition was dependent on the sumultaneous oxidation of the molecule. However, the amount of energy transferred in an argon plasma may be rate-controlling, and was not determined.

In order to ascertain whether the "silicon-oxygen specie" could be formed entirely in the vapor phase, tetraethylsilane, $(C_2H_5)_4Si$, was decomposed in an oxygen plasma. It was found that the silica films deposited in this manner were indistinguishable from the silica films formed

from $(C_2H_5O)_4Si$. The refractive indices and infrared adsorption spectra were similar; the apparent heats of adsorption on platinum were also the same, as determined from the temperature dependence of the deposition rate, which is shown in Figure 6. With a $(C_2H_5)_4Si$ evaporation rate of 0.08 cm^3/hour, the deposition rate of silica on a platinum foil kept at 306°C was 4.15 x 10^{-4} mg/cm^2 minute. Under similar conditions, the deposition rate with $(C_2H_5O)_4Si$ was 6.9 x 10^{-4} mg/cm^2 minute. These deposition rates are not too different. It was concluded, therefore, that the "silicon-oxygen specie" which formed the Si-O-Si network could be synthesized directly in the vapor phase. Since the deposition of silica was possible in an argon plasma, it is reasonable to suspect that the main role of an oxidizing atmosphere was to remove the hydrocarbon portions of the metal-organic molecule.

Based on the foregoing experiments, the following mechansim is proposed for the growth of a silicon dioxide film: The metal-organic molecules and energized oxygen species enter the reaction furnace and collide. As a result, some of the metal-organic molecules absorb sufficient energy to cause bond rupture. A simultaneous oxidation of the hydrocarbon portions of the molecule

assists the decomposition process and "silicon-oxygen species" are rapidly formed in the gas phase. Each specie is then imagined to possess a mean life-time in which to select a site on the substrate and become physically adsorbed. The Si-0-Si network is formed when additional "silicon-oxygen species" are adsorbed. These species are not necessarily SiO_2 molecules, but may correspond to "free radicals" of the type SiO, SiO_3, or SiO_4, which are directly available from the organic molecule. The adsorbed "radicals" may then crosslink to form a network of SiO_4 tetrahedra, and the overall composition of the film deposited would correspond to SiO_2. As previously mentioned, the refractive indices and infrared adsorption spectra of all silica films deposited in this study were similar to the same properties of silica glass formed by fusion and subsequent cooling. Silicon dioxide always forms a network, whether it is crystalline quartz, cristobalite, tridymite, or a glass. It appears that the network is structurally the most stable form of the solid.

CONCLUSIONS

1. Non-crystalline SiO_2 films can be deposited at low temperatures by the decomposition of tetraethoxysilane

in a gaseous plasma produced with a glow discharge. These films are structurally similar to silica glass prepared by conventional fusion techniques, as evidenced by their infrared absorption spectra and refractive indices.

2. The decomposition of tetraethoxysilane in an oxygen plasma produces extensive water. This water can be chemically incorporated into the oxide films when the substrates are held below a certain temperature, which depends on the organic flow rate.

3. The decomposition of tetraethoxysilane in an oxygen plasma obeys a first order rate law at 250 microns pressure and temperatures near 300°C.

4. The deposition rate of silica is directly proportional to the $(C_2H_5O)_4Si$ evaporation rate below a limiting value, which is dependent on the available surface area of the substrate and its temperature.

5. The "silicon-oxygen species" which form the silica network are physically adsorbed by the substrate below 410°C. The apparent heat of adsorption of silica on NaCl, Pt, or fused SiO_2 is 12.7 ± 0.2 kcal/mole. The apparent heat of adsorption on Al_2O_3 or Al is 9.5 ± 0.3 kcal/mole. The difference in the apparent heats

of adsorption is of silica most likely due to the incorporation of hydroxyl groups into the silica film deposited on the alumina or aluminum substrates.

ACKNOWLEDGEMENTS

Figure Captions

Figure 1.   Schematic Drawing of Glow Discharge Apparatus.

Figure 2.   Comparison of the Infrared Absorption Spectra
            of a Noncrystalline Silica Film Prepared by
            Vapor Deposition, and Fused Silica Glass.

Figure 3.   Linear Relation of Silica Deposition with Time.

Figure 4.   Relation of Logarithm Silica Deposition Rate
            and 1/T for Deposition on Various Substrates.

Figure 5.   Relation of Silica Deposition Rate and
            Tetraethoxysilane Evaporation Rate.

Figure 6.   Relation of Logarithm Silica Deposition Rate
            and 1/T for Noncrystalline Silica Films
            Prepared by the Vapor Phase Decomposition
            of Tetraethoxysilane and Tetraethyl silane.
            (Deposition on Platinum Foil).

REFERENCES

1. D. R. Secrist and J. D. Mackenzie, Glass Industry 45, (8), 408-13 (1964).

2. L. L. Alt, S. W. Ing, Jr., and Karl W. Laendle, J. Electrochem. Soc. 110, 465 (1963).

3. S. W. Ing, Jr., and W. Davern, J. Electrochem. Soc. 112, (3), 284 (1965).

4. Progress in Reaction Kinetics, Chap. 1, p.29, edited by G. Porter, Pergamon Press, New York, 1961.

5. S. Dondes, private communication, R.P.I., Troy, N. Y.

6. D. R. Secrist and J. D. Mackenzie, Solid State Electronics 9, 704-705 (1966).

7. J. D. Mackenzie, J. Am. Ceram. Soc. 46, (10), pp. 461-470 (1963).

8. I. Simon, Chap. 6 in Modern Aspects of the Vitreous State, Vol. 1, edited by J. D. Mackenzie, Butterworth & Co., Ltd., London, 1960.

9. W. A. Pliskin and H. S. Lehman, J. Electrochem. Soc. 112, (10), 1013-1019 (1965).

10. E. L. Brady, J. Phys. Chem. 57, 706 (1953).

11. F. G. Straub, University of Illinois Engineering Experimental Station, Bull. Series 364 (1964).

12. L. Brewer and G. R. B. Elliott, Ph.D. Thesis, University of California, Berkeley, 1952.

13. J. A. Hockey and B. A. Pethica, Trans. Faraday Soc. 57, 2247 (1961).

14. J. Klerer, J. Electrochem. Soc. 112 (5), 503 (1965).

15. S. Brunauer, The Adsorption of Gases and Vapors, Vol. 1, Physical Adsorption, p. 245, Princeton University Press.

16. See Reference 15, p. 244.

17. J. W. McBain, Colloid Science, p. 76, D. C. Heath and Co., Boston, 1950.

18. J. B. Peri and R. B. Hannan, J. Phys, Chem. 64, 1526 (1960).

19. A. A. Frost and R. G. Pearson, Kinetics and Mechanism (2nd ed.) Page 262, John Wiley & Sons, Inc., New York, 1961.

20. T. L. Cottrell, The Strengths of Chemical Bonds, Chap. 8, p. 160, Academic Press, Inc., London, 1958.

Figure 1. Schematic Drawing of Glow Discharge Apparatus.

Figure 2. Comparison of the Infrared Absorption Spectra of a
Noncrystalline Silica Film Prepared by Vapor
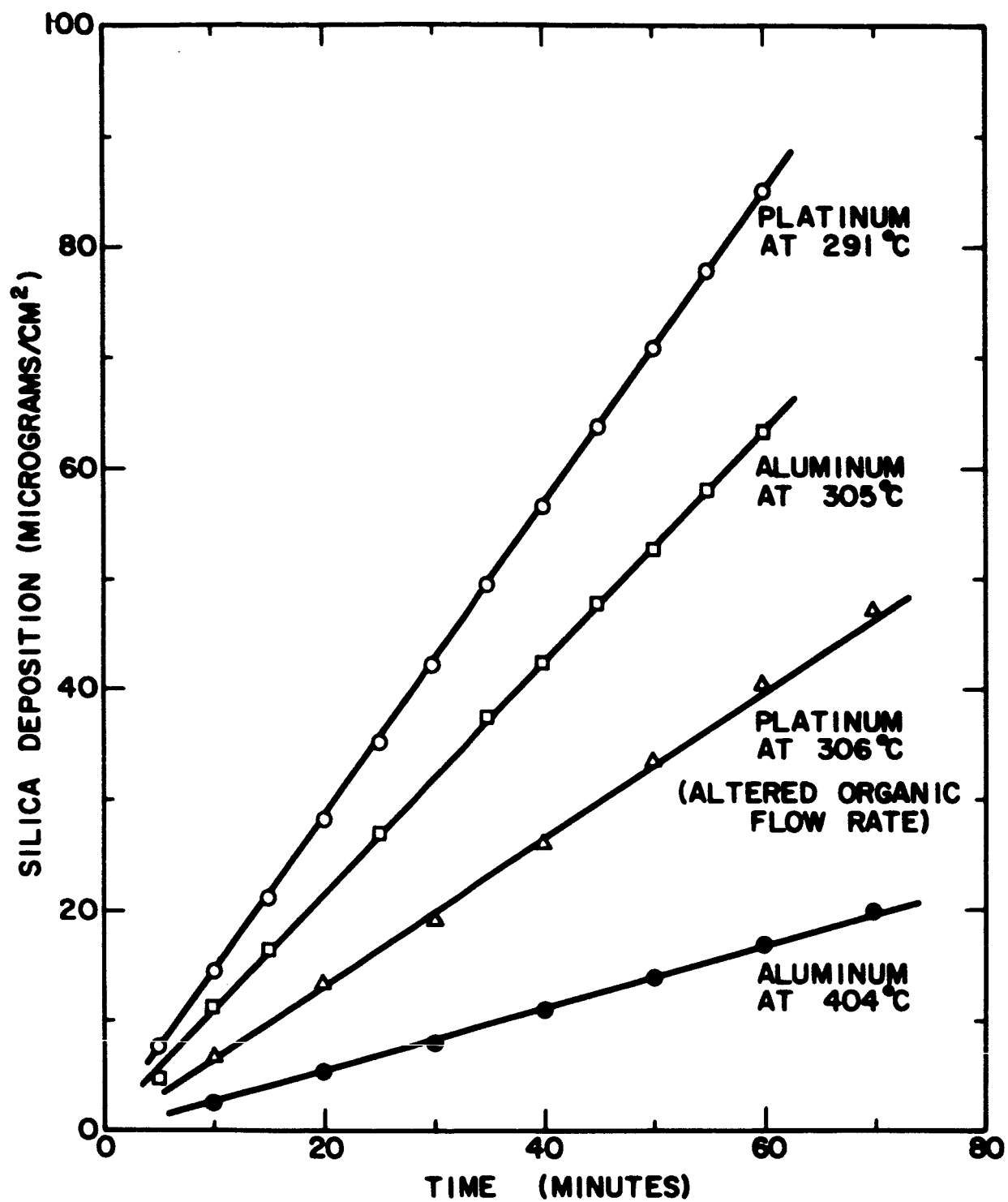Deposition, and Fused Silica Glass.

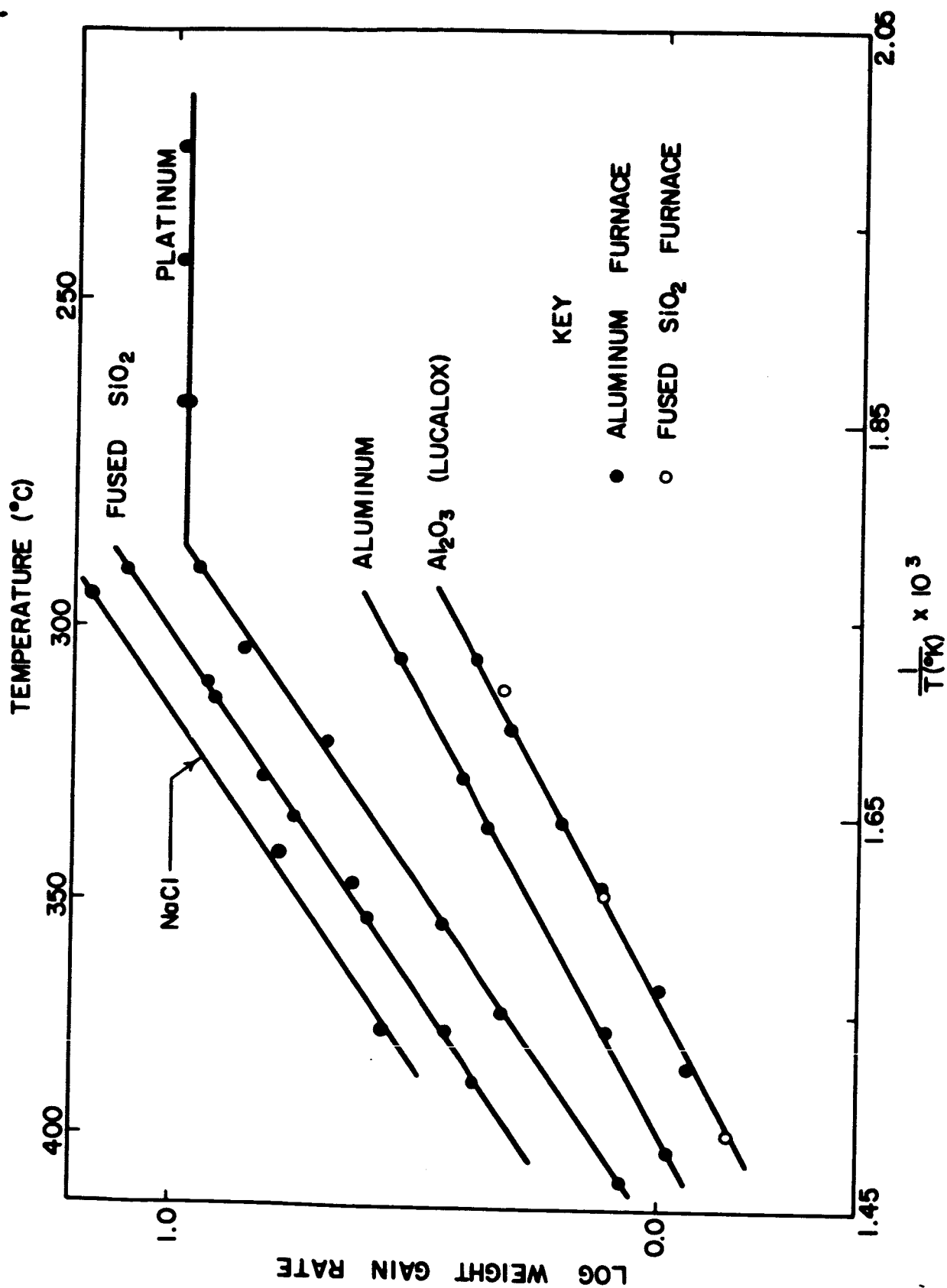Figure 3. Linear Relation of Silica Deposition with Time.

Figure 4. Relation of Logarithm Silica Deposition Rate and 1/T for Deposition on Various Substrates.
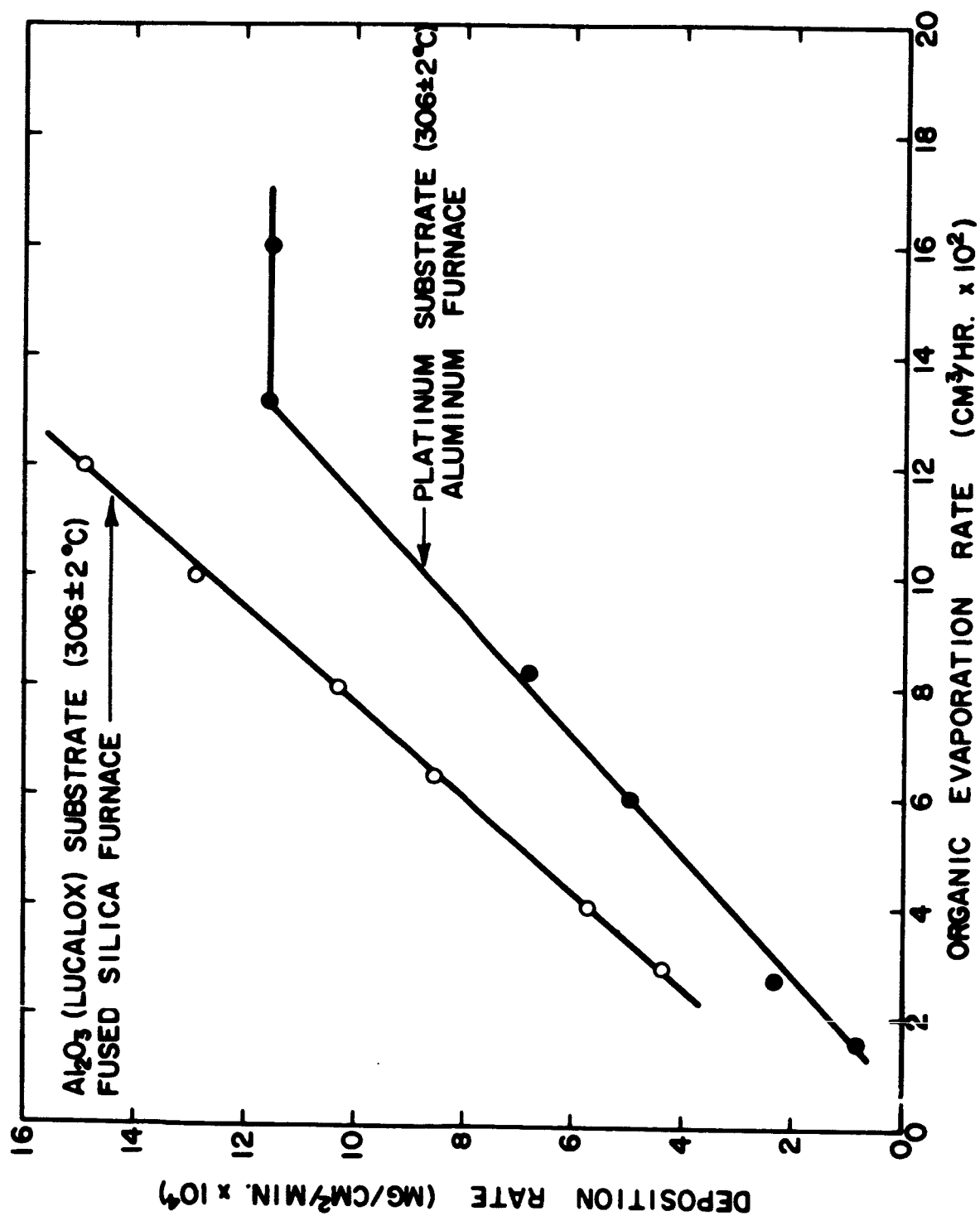
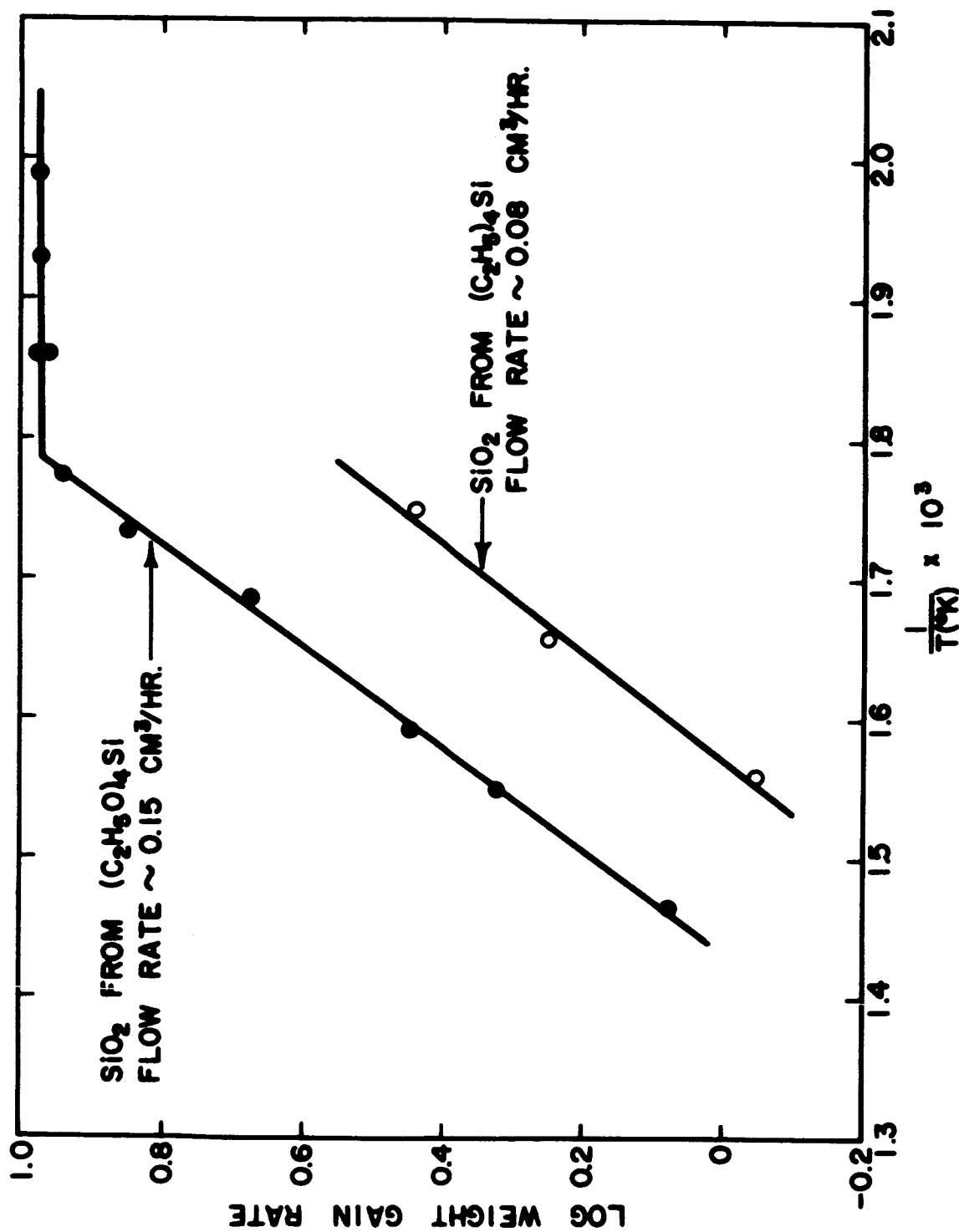Figure 5. Relation of Silica Deposition Rate and Tetraethoxysilane Evaporation Rate.

Figure 6. Relation of Logarithm Silica Deposition Rate and
1/T for Noncrystalline Silica Films Prepared by
the Vapor Phase Decomposition of Tetraethoxysilane
and Tetraethyl silane. (Deposition on Platinum
Foil)